

Standard Operating Procedure for Coating Annular Denuders with XAD-4 Resin

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1.0 Purpose

To prepare clean, stable, high capacity sorbent coatings for trapping gas phase SVOC on glass annular denuders

2.0 Background

Annular denuders are to be incorporated into the Versatile Air Pollution Samplers (VAPS) for evaluation of their ability to remove semi-volatile organic compounds species from the ambient air before it is drawn through a filter that will be used to quantitate particulate carbon. This Standard Operating Procedure explains how such annular denuders are coated with the sorbent resin XAD-4 for use in the VAPS. This procedure can be adapted for coating denuders of other dimensions and geometries by adjusting the quantities of materials to scale with the surface area of the denuders.

3.0 Facilities

- Laboratory hood
- Source of clean dry nitrogen, clean tubing and fittings to bring N₂ to the hood
- (Optional: House vacuum at the laboratory hood, at the facility where solvent extracts of the exposed denuders are to be analyzed for organic species.)

4.0 Supplies

- Aluminum foil
 - Solvents for denuder coating and extraction, distilled in glass or pesticide grade: Hexane, dichloromethane, acetone
 - Solvent for preparation of cleaning solution: Ethanol or methanol as available
 - Beakers (4) for holding the coating slurry: 500 mL (or 2.5 x the slurry volume)
 - Beakers: 600, 200, 100 mL, several of each
 - Laboratory scoop for weighing XAD
 - Blunt end tweezers such as used for handling air sampling filters
 - Laboratory wipes (Kimwipes)
 - Potassium or sodium hydroxide pellets for preparation of the glassware cleaning solution
 - Glass rods for stirring the slurry and for directing the flow of the slurry into the denuders
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5.0 Equipment:

- Ultrasonic bath, large enough to hold two 500 mL beakers at the same time
- Top-loading pan balance ± 0.002 g

6.0 Worker protection

- Protective gloves that are suitable for contact with hexane
- Lab coat
- Viton gloves for resistance to the alkaline cleaning solution
- Safety glasses
- Masks or respirator (activated carbon cartridges to trap hexane and filter for fine particles)

7.0 Advance preparations

A. Assemble supplies and equipment

B. Prepare the laboratory space

- Refer to the list of materials and supplies.
 - Make sure that the hood ventilation system works and that there is at least one square meter of unobstructed surface. Cover the hood with lab absorbent paper or Al foil (so that any splatter of slurry can be cleaned up easily). At minimum, a 'clean' area of 30 x 30 cm, covered with clean Al foil or clean Kimwipes, should be designated for lay down of beakers, glass rods etc.
 - Put the sonic bath into the laboratory hood, add at least 2 cm of water, and plug it in.
 - Prepare about twenty 12 by 12 cm squares of aluminum foil by rinsing with hexane on both sides and air drying or heating in a muffle furnace to 500°C. These are used to cover the beakers and denuder tube ends, and for other purposes.
 - Clean the glassware with ethanolic (or methanolic) NaOH or KOH, rinse thoroughly with deionized water, air dry. Invert the glassware while it is drying, or cover loosely with Kimwipes to prevent deposition of airborne particulate matter. When it is dry, store in a clean area or cover each piece with clean aluminum foil.
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8.0 Denuder Coating

- Prepare hexane-XAD-4 slurries: Weigh 1.30 g ground XAD-4 resin into a clean 400 mL beaker. Use a dust mask that filters out particles down to 0.5 micrometers. Take the beaker to the hood, add 200 mL UV (pesticide analysis) grade hexane. Cover with clean Al foil. Place the beaker into the sonic bath and turn it on. Sonicate at room temperature for at least 30 min. It is OK if the bath water gets warm (to 40°C) from the heat of the sonicator's continuous operation. The slurry must be suspended in order to coat the denuder surfaces evenly. While the slurries are sonicating, clean the end pieces, the Teflon-coated aluminum connectors that attach the denuders to the VAPS. Prepare one slurry for each denuder. Label the slurry beaker with its denuder ID.
 - Before coating any denuders that have removable end pieces: Practice attaching the end pieces. Use a foam cradle or similar cushion for support of the midsection of the denuder. Each end piece should have two o-rings of about 5 cm diameter inside the wider end. These should have very light grease coating that is barely perceptible to an ungloved finger. To attach, be careful to keep the end piece and denuder co-axial. Slide the end piece on gently, with slight twisting, if necessary, to minimize bumping the glass denuder end into the aluminum step of the end piece. With careful attention to pressure sensations in the fingers that hold the end cap and denuder, notice the ease of sliding the piece on until it makes contact with the first o-ring. Sliding requires a little more effort until the glass reaches the second o-ring. Even more effort is required to move the glass over the second o-ring, and it is possible to overdo this and bang the glass into the step at the end of the end piece barrel. Slight twisting while pushing helps to minimize this impact.
 - Measure the depth of the denuder inside the end cap. Record this length. Attach the other end piece.
 - Before coating any denuders that have removable end pieces: Practice removing the end pieces. Put a foam cushion section, about 10 cm in length, such as used for pipe insulation, around the middle of the denuder. Pull the end pieces off gently, one at a time. By monitoring the force needed to move the end piece, it is possible to sense the glass passing over the first and then the second o-rings. Avoid jerky motions to prevent damage to the glass ends of the denuders. If the end piece is difficult to remove, twist while pulling, so as to minimize sudden increase in pressure or banging the metal and glass together.
 - When the end pieces need to be cleaned (for example, between coatings of different denuders, and after field use): Remove the end pieces from the denuder. Remove the 5 cm diameter inner o-rings by carefully pulling/rolling, one at a time, so that the bulging o-ring can be rolled out by hand. Alternately, wedge them out one at a time, using blunt-end tweezers or the round end of a scoop. Do not use tweezers or forceps with pointed ends, as they will scratch the end
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pieces or damage the Teflon coated aluminum surface of the end piece. Wipe out the o-ring grooves with a Kimwipe; follow with another that has been prewet with hexane. Remove the small o-ring from the smaller diameter end only when the end piece is to be cleaned with hexane.

- With o-rings and gaskets removed, the end pieces can be sonicated in hexane, air dried, and then sonicated again in methanol or other solvent. At a minimum, rinse each end piece with hexane from a squirt bottle and air dry. Air dry on the clean area in the hood. Wrap with clean aluminum foil if the end piece is to be stored.
 - Wipe the o-rings with Kimwipes. Check for nicks, dust, grit, XAD resin or other visible contamination. Make sure that the o-rings have a very light coating of high vacuum silicone stopcock grease. Re-insert the o-rings, taking care not to spread the grease around on the inside surface of the end piece.
 - Attach the end pieces to the denuders, making sure that the second o-ring has reached the glass. Check the depth of the denuder inside the end cap. If the depth is greater by 5 mm than the depth measured in step 3, gently rotate the end cap while applying pressure so that the o-rings will slide smoothly over the glass.
 - Pour 500 mL hexane into a clean beaker. Rinse the assembled denuder twice with hexane to clean: Put a threaded Teflon plug into the open end of one end cap. Hold the denuder vertical, resting on the end cap, and support it in a padded clamp attached to a ring stand. To avoid hexane contact with the small o-ring in the end piece, put a clean glass rod into the open end of the denuder, past the small o-ring, and use it to guide hexane into the denuder annuli. Fill about half way. The volume depends on the design of the end piece. (The denuder designed for the VAPS in 1998 has an internal volume of about 180 mL.) This requires about 500 mL for the denuders and end pieces available in November 1998. Cap the denuder end piece. Carefully unclamp the denuder and support it with one hand at each end. Invert 20 times (10 complete revolutions) with one quarter turn axial rotation for each inversion. Remove one end cap and pour out the hexane rinse into a waste beaker while supporting and rotating the denuder. Remove the other Teflon end plug and air dry the denuder (horizontally) in the hood. (Keep the end pieces in place on the denuder).
 - Apply slurries to the annuli: When the denuder is dry, as indicated by the movement of the solvent front through the denuder, put a Teflon plug on one end piece and support the denuder in the ringstand. Carefully place the clean glass rod into the opening of the end piece, so that it rests on the denuder annuli. Make sure the slurry is still sonicating. Turn off the sonicator, remove the beaker, touch the underside of the beaker to a paper towel or tissue to remove water from the sonic bath. Let the slurry settle, but for no more than 15 sec before pouring it along the glass rod into the denuder. Add about 80% of the slurry volume to the denuder. The
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remainder should be reserved in the beaker. (If all the slurry is added, a streaky, uneven coating may result because of the presence of larger than optimal particles.) Cap the top end of the denuder, remove the denuder from the clamp, support in both hands and invert 20 times.

- Decant the slurry into its beaker by pouring while rotating the denuder. Rotate the denuder to minimize the formation of streaks in the coating. Top up the slurry volume to 200 mL with clean hexane, cover the beaker with clean Al foil and return it to the sonicator. Continue to sonicate between coating steps.
 - Remove the second white cap from the denuder. Place the denuder on the bench of the hood so that it is perpendicular to the back wall, about two inches from the wall. Dry the denuder in the laboratory hood between coatings. Air drying will take about 10 minutes. As the solvent front evaporates the appearance of the denuder changes. Rotate the denuder once or twice while the hexane is evaporating. Alternately, clean (ultrapure) dry nitrogen can be used to dry the denuder between coatings. However, the source purity needs to be verified before routine use for denuder drying, because the XAD coating will adsorb any organic impurities from the drying gas.
 - Re-apply the slurry. Repeat steps 10-12 at least 7 times. Collect the slurry residue and let the hexane evaporate. Dry used XAD from all the denuders should be saved and returned to L. Gundel or D. Lane for re-grinding.
 - After the final coating step, rinse the coated denuder twice with clean hexane to remove loose resin particles. Put the white cap on one end. Add about 200 mL hexane to the denuder when it is mounted vertically in the ringstand. Attach the other cap, remove from the ringstand and invert 20 times with twisting, as in denuder coating. Pour the rinse to waste while turning the denuder. Air dry and repeat.
 - Before the denuder has dried completely after the second rinse remove the end pieces, using the techniques that were practiced in step 4. Wet a Kimwipe with hexane and wipe off any remaining stopcock grease from the outside of the denuder ends.
 - Remove coating from the last 0.5 cm of each end of the denuder. The purpose of this step is to make sure that the adhesive joints between the inner tubes do not have patches of XAD resin that could flake off during sampling. Use a beaker that is wide enough to fit the cross section of the exposed glass end of the denuder. Add hexane to the beaker to about 1 cm depth. Put the beaker into the sonicator and turn it on. Carefully hold the exposed end of the denuder into the beaker so that just the bottom 0.5 cm is below the hexane level, but do not let the denuder rest on the bottom of the beaker. Sonicate for 15 sec. Lift the denuder up to inspect the end. Repeat. Apply the same procedure to the other end of the denuder. Air dry the denuder. It should be possible to see where the coating has been removed from each end.
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- When the denuder is dry, carefully cap the exposed ends with clean aluminum foil and wrap the whole denuder twice with aluminum foil. Roll the denuder with bubble wrap and put it into a cardboard box for storage before shipment. When Teflon end caps become available these should be used instead of the aluminum foil. (Before use caps should be cleaned with hexane after the o-rings have been removed and the grooves wiped clean with Kimwipes.

9.0 Extraction of Coated Denuders Before Field Use

1. Attach end pieces
2. Extract coated denuders with specified solvent mixture
3. Seal denuders for airtight storage
4. Keep the denuders in secure storage until use.
5. Extract each denuder with the specified solvent mixture for blank on the day (of or before) sampling
6. Archive the extract

10.0 References

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L.A. Gundel, V.C. Lee, K.R.R. Mahanama, R.K. Stevens and J.M. Daisey, Direct determination of the phase distributions of semi-volatile polycyclic aromatic hydrocarbons using annular denuders, Atmos. Environ. 29, 1719-1733 (1995).

11.0 Abbreviations

LBNL	Ernest Orlando Lawrence Berkeley National Laboratory
SVOC	Semi-volatile organic compounds
VAPS	Versatile Air Pollution Sampler
